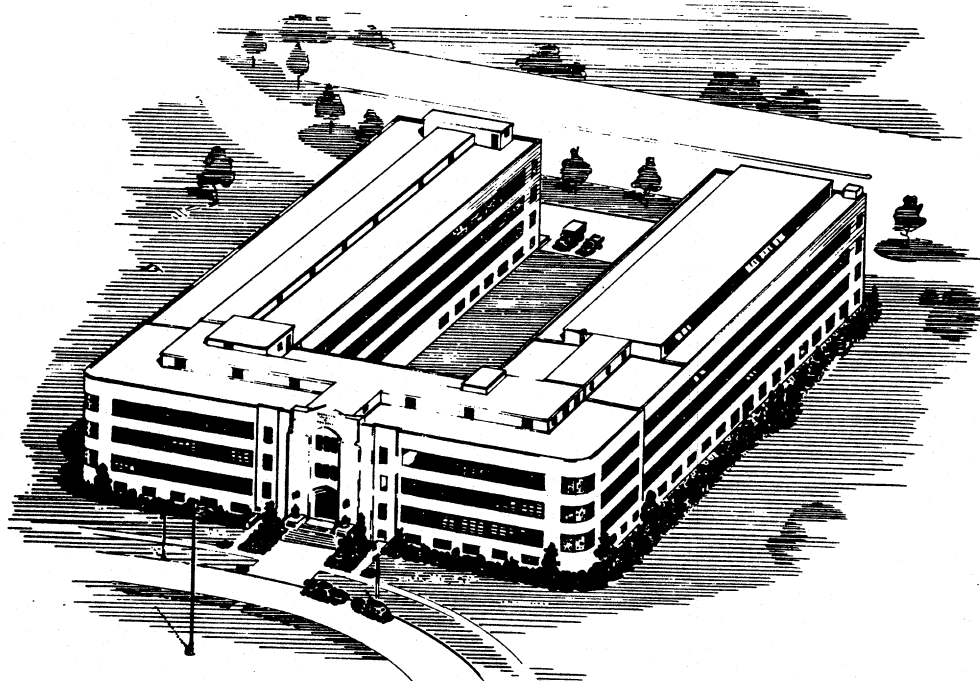


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ALLYL STARCH--A REVIEW

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While starch is insoluble in organic solvents and forms only a paste (colloidal solution) with water, a number of starch derivatives, particularly esters and ethers, are soluble in organic solvents and possess properties entirely different from those of the original starch. One ester, nitrostarch, proved to be of practical value as an explosive. In this review the work on the preparation and properties of an ether of starch containing an unsaturated radical--allyl ether of starch--is described.

### Preparation of Allyl Starch

The earliest reference to allyl starch in the literature is that by Tomecko and Adams (66) who prepared what they called a "monoallyl starch" (one allyl group per maltose unit) by direct reaction of starch with allyl bromide in the presence of 10 percent aqueous sodium hydroxide. The product was slightly soluble in alcohol and glacial acetic acid, insoluble in ether. Repetition of Tomecko and Adams' experiments in this Laboratory gave a similar product (0.5 allyl group per glucose unit) which was only slightly soluble in water and practically insoluble in acetone, ethylene chlorohydrin, and other organic solvents. It is obvious that the substitution obtained is entirely too low to make a product distinctly soluble in organic solvents (38).

A clue to the explanation of low substitution in the product obtained by Tomecko and Adams was found in the fact that no allyl bromide could be recovered in spite of the large excess used (85 to 10 grams starch or a mole ratio of 11 to 1). This was attributed to two side reactions which parallel the main reaction of etherifying the hydroxyl groups. The allyl bromide is hydrolyzed by the alkali to allyl alcohol, and this reacts with allyl bromide to form allyl ether. The hydrolysis of allyl bromide and also of allyl chloride (used in later experiments) at various temperatures and with various concentrations of alkali was therefore investigated. Equal volumes of allyl bromide or chloride and sodium hydroxide solution were mixed and stirred at various temperatures for 3 hours. At 80° C. (approximately the temperature of the reaction for the preparation of allyl starch) the results were as follows: With alkali concentrations up to 10 percent, about 23 percent of allyl bromide was hydrolyzed<sup>1/</sup>, with 20 to 30 percent alkali, about 9 percent; and with 40 to 50 percent, only about 2.5 percent. About 21 percent allyl chloride was hydrolyzed with 10 percent sodium hydroxide, and only about 1 percent with 40 to 50 percent alkali. These experiments pointed to the advisability of using higher concentrations of alkali in the preparation of allyl starch.

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1/ AT CONCENTRATIONS UP TO 10%, THE ENTIRE AMOUNT OF ALKALI WAS USED UP, AND THEREFORE 23% REPRESENTS THE MINIMUM HYDROLYZED.

A good laboratory method for obtaining organic solvent-soluble allyl starch with the substitution of about two allyl groups per glucose unit is one similar to that used by Haworth, Hirst, and Webb (33) for methylation of starch--that is, simultaneous hydrolysis and allylation of starch acetate in acetone solution. This method is carried out as follows (30, 38, also 35). In a flask fitted with a mechanical stirrer and reflux condenser, 100 grams of starch acetate are dissolved in 250 cc. of acetone, 250 grams of 50 percent aqueous sodium hydroxide and 300 cc. of allyl bromide are added, and the mixture is heated at reflux temperature for 3.5 hours. The volatile portion of the reaction mixture is then removed rapidly (15 minutes) by distillation with steam, the gummy product remaining in the flask is washed until alkali-free, and it is then dissolved in about 150 cc. of acetone. When this acetone solution is poured into rapidly stirred water at room temperature, nearly white gummy allyl starch is obtained. The yield is about 90 grams of the gum, containing about 20 percent of water. An appreciable proportion of the allyl bromide used can be recovered from the steam-distilled liquid. The same compound can be prepared using cheaper allyl chloride instead of allyl bromide, but because of the low boiling point of allyl chloride (45° C.) the reaction must be carried out in an autoclave at 80° C. for about 11 hours.

For obtaining larger quantities of allyl starch the following direct allylation method is more economical (38, 43, also 35, 41): Five hundred grams of air-dry starch is stirred into 2000 grams of 50 percent aqueous sodium hydroxide in a glass-lined or stainless steel autoclave at room temperature, and 2500 cc. of acetone and 3000 cc. of allyl chloride are added with constant stirring. The autoclave is heated at about 86° C. (approximately 30 pounds pressure). The liquid is then distilled with steam for about 40 minutes to remove the acetone and excess of allyl chloride. The separated gum is washed with water until free of alkali. The gum can be further purified by dissolving in acetone, filtering off the small amount of unchanged or lowly substituted starch (less than 3%), and precipitating with water. Acetone, allyl chloride, and allyl ether can be recovered from the distillate. The results of several runs are given in Table I. They were obtained with the laboratory equipment available and do not represent the optimum yields and recovery of solvent.

This table shows that for most ordinary starches the reaction time is about 10 hours; for waxy maize starch, which consists entirely of amylopectin, it is 20 hours; for a starch-degradation product such as dextrin, it is 4 hours. The yields are given on a wet basis (20-25% moisture).

Starch can be allylated directly with allyl bromide without the use of an autoclave provided a solvent of higher boiling point than acetone is used, such as methylethyl ketone or even an excess of allyl bromide. Thus, Nichols, Meiss, and Yanovsky (43), on refluxing the mixture of 50 g. starch, 300 g. allyl bromide, 100 g. sodium hydroxide, 67 cc. water, and 250 cc. methylethyl ketone for 10 hours, obtained a product with 2.2 allyl groups per glucose unit. Chadapaux, Champetier, and Savostianoff (9, 10) used a mixture of 100 g. potato starch, 600 cc. allyl bromide, 400 g. of 50 percent solution of sodium hydroxide, and 500 cc. methylethyl ketone. They obtained allyl starch with about two allyl groups per glucose unit on heating this mixture at 69-75° C. for 40 to 50 hours. The reaction time can be reduced if more soluble potassium hydroxide is substituted for sodium hydroxide in the above mixture thereby also reducing the amount of water present. Their results are given in Table II.

TABLE I. PREPARATION OF ALLYL STARCH (38)

Material Used	% Mois- ture	Reaction Time, Hr.	Yield Grams	Yield Cor. Moisture	Yield, % of Theo- retical	% Allyl Content (Wijs Method)	Allyl Groups per Glu- cose Unit	Grams Recovered Allyl chloride	Allyl ether
Potato starch	16	11	860	612	93	37.0	2.3	795	94
Potato starch	16	11	890	620	94	37.1	2.3	1213	79
Sweet potato starch	14	10	900	603	99	30.0	1.7	924	117
Cornstarch	12	10	986	684	98	37.4	2.4	770	72
Cornstarch	12	10	972	676	96	37.5	2.4	882	105
Tapioca starch	13	9	830	617	92	35.0	2.1	823	93
Waxy maize starch	10	20	900	617	92	33.5	2.0	460	68
Standard tapioca dex- trina	3	4	816	646	89	33.2	2.0	1262	89

<sup>a</sup>Viscosity, 8.5 centistokes in 50% solution at 130° F.

TABLE II

PREPARATION OF ALLYL STARCH FROM POTATO STARCH [CHADAPAUX et al (10)]

<u>Solvent</u>	<u>Concentr. of KOH solution added, %</u>	<u>Reaction Temperature, °C.</u>	<u>Duration of Reaction (hrs.)</u>	<u>Allyl Content, %</u>	<u>Allyl groups per glucose unit</u>
Methylethyl ketone	58	68-71	16	32.0	1.83
" "	58	68-71	18	33.5	1.96
" "	58	68-71	20	34.4	2.04
" "	65	70-75	11	33.4	1.95
" "	65	70-75	13	33.7	1.98
" "	65	70-75	17	33.5	2.14
" "	67	70-73	12	32.7	1.90
" "	70	69-73	11	32.6	1.89
" "	72	72-74	15	32.6	1.89
" "	75	71-75	13	32.8	1.90
" "	75	71-75	18	34.0	2.02
Allyl bromide	70	70-74	15	35.7	2.16
" "	70	70-74	17	35.8	2.22

All the methods for preparing allyl starch described thus far had one feature in common. A very large excess of allyl chloride (or bromide) was used in all of them. And while it is true that some of the allyl halide can be recovered as such, part of it is recovered as diallyl ether (a substance of no known use at present), or as water soluble allyl alcohol. If allyl starch is to be a product of practical importance in a competitive field of resins or plastic compositions, a more economical method for preparing it had to be developed. Such a method would postulate the use of allyl chloride instead of allyl bromide, thereby reducing the rate of the reaction. The excess of allyl chloride should be reduced very considerably. This would further reduce the rate of the reaction and would tend to decrease the degree of substitution. For practical purposes the substitution should be between 1.7 and 2.0 allyl groups per glucose unit.

As a matter of fact, when the amount of allyl chloride used in the reaction was reduced from about 600 percent excess (as in the method described above) to about 100 percent excess, it took between 30 and 40 hours to complete the reaction, and at the end the substitution was about 1.6 allyl groups per glucose unit. Dozens of experiments in which the ratio starch allyl chloride: sodium hydroxide was varied within wide limits led eventually to a more economical method for preparing allyl starch, using a comparatively slight excess of allyl chloride. The method is based on the following findings. Allylation of starch is a distinctly exothermic reaction. If samples of reaction mixture are taken at various intervals of time, it will be found that soon after the exothermic phase of the reaction has subsided (after two or three hours) the product will have about the same degree of substitution as the one isolated several hours later. The earlier sample, however, will be allyl starch of very high molecular weight and insoluble in organic solvents. On further heating a breaking down of allyl starch takes place until it reaches the molecular weight value at which it becomes soluble in organic solvents, which is in the neighborhood of 15,000-20,000 (32). It appears, therefore, that during the course of the reaction of allyl starch formation more time is required for breaking down the allyl starch of high molecular weight than for producing allyl starch itself. It was found, however, that the depolymerization of allyl starch can be expedited by the addition of some acid to the reaction mixture.

The method as finally adopted is as follows (31, 61): The preparation of allyl starch was carried out in a two-gallon glass-lined laboratory kettle with a closed anchor-type stirrer. The stirrer was driven through a reducer by a 1/3 horsepower motor at a rate of 55-60 r.p.m. The jacket of the reaction vessel was piped so that either steam, cold water, or hot water could be circulated through it.

The general method was to paste air-dry potato starch (875 g., 13% moisture) with 980 g. of 50 percent sodium hydroxide solution. The alkali solution could be prepared in the reaction kettle and cooled to below 30° C. and then the starch could be mixed in, or the starch could be put in the kettle first and the cooled alkali solution then added. After the starch was thoroughly pasted, allyl chloride (985 g., 37% more than theoretical for two allyl groups) and acetone (3-5 liters) were added. The kettle was closed and heated to the operating temperature with steam (15-20 min.), and then hot water was circulated through the jacket to maintain the reaction mixture at about 90° C. The material showed signs of reaction

when the temperature reached 50-60° and the lower starch layer began to mix with the upper organic layer. The pressure rose to about 40 pounds and then began to decrease gradually. After 3-5 hours the mixture became a thick, semisolid paste. After about 10 hours (continuous heating or allowing the kettle to cool to room temperature overnight), the kettle was cooled and opened. The pH (Hydrion paper) of the mixture ranged from 7 to 9 at this stage. Sufficient concentrated hydrochloric acid (30-40 cc.) mixed with acetone was added to bring the pH to 3 or slightly lower. Then the kettle was closed and heated to the reaction temperature and held there until the doughy material dissolved, which required about an hour. At this point the salt settled if the stirrer was stopped. After the material was in solution, the kettle was cooled by circulating cold water. The solution was then removed by siphoning it with suction into the 3-gallon bottle used for steam distillation. The mixture was steam distilled to remove the solvent, excess allyl chloride, and the volatile byproducts of the reaction. The doughy mass obtained was kneaded with warm (40-60° C.) running water to wash out the salt. The gummy material can be purified by dissolving it in acetone and precipitating the filtered solution with several volumes of water. Approximately 80 percent of the acetone used could be recovered from the steam distillate. Ten batches of allyl starch made by this method gave an average yield of 937 g. or 86 percent of theory, of gummy material (on dry basis). The average substitution was 1.65 allyl groups per glucose unit.

The addition of 1 percent of sodium iodide (based on the weight of starch) improved somewhat the substitution of the final product. For ten experiments the average yield was 957 g., or 87 percent, and the substitution, 1.8 allyl groups per glucose unit. Increasing the amount of alkali from 490 g. to 540 g. (with sodium iodide present) increased the substitution to 1.9 groups and the yield to 90 percent (990 g.) (average of five experiments). Larger amounts of acid were needed for solubilization of the product at the end of the reaction (about 100 cc.).

To avoid the use of the autoclave, a similar procedure for making allyl starch by the use of allyl bromide instead of allyl chloride and methylethyl ketone instead of acetone has been developed. Only about 14 percent excess allyl bromide is required to obtain a product containing 1.8 allyl groups per glucose unit (61).

#### Other Modifications of the Preparation of Allyl Starch (61, 63, also 34)

Two side reactions are known to take place during the preparation of allyl starch described above. Hydrolysis of allyl chloride in the presence of alkali has been discussed and the situation has been taken care of, at least in part, by the use of concentrated alkali solution. The other side reaction is the one between the alkali and the acetone used as a solvent, which results in the formation of mesityl oxide and other condensation products of acetone. Although formation of the acetone condensation products does not affect adversely the preparation of allyl starch, it complicates the recovery of the solvent. Substitution of methylethyl ketone for acetone, a slightly more expensive but less reactive substance, reduces the amount of side products formed. However, complete elimination of ketones



might be desirable. Toluene has several advantages over acetone. It is inexpensive, unreactive under the conditions of the experiment, immiscible with water (which facilitates separation of the final products), and readily recovered. On the other hand, the immiscibility of toluene with water retards the reaction somewhat, and requires better stirring facilities. When the batches were made with allyl bromide in a glass flask, in which good stirring was available, products of good substitution were obtained. In our autoclave the stirring was slower and less efficient, which slowed down the reaction considerably when toluene was used as a solvent. It required about 15 hours to bring the reaction mixture to pH 7, and it required several hours more to dissolve the product after addition of acid. The substitution of allyl starch prepared in this manner was 1.5 allyl groups per glucose unit.

It seems that the presence of acetone or other solvent in the reaction mixture was a twofold function. Perhaps its most important role is to dissolve the allyl starch after the allylation has been completed. Besides, the presence of the solvent moderates the markedly exothermic reaction of etherification. A number of preparations have been made without solvents during the reaction in the following manner. In all these experiences, 50 percent excess allyl chloride was used instead of 37 percent.

A smooth paste was made with 800 g. of air-dry starch and 980 g. of 50 percent sodium hydroxide at room temperature. To this paste one percent of sodium iodide and 985 g. of allyl chloride were added, and the mixture was slowly heated in the closed autoclave. The reaction started before the mixture reached the usual temperature of reaction ( $90^{\circ}\text{C}.$ ). The pressure rose to about 60 pounds. On further heating at  $90^{\circ}$ , the pressure gradually dropped to 15-20 pounds, indicating that the reaction was over. This required about four hours. At this point acetone (3-5 liters) and hydrochloric acid (40-50 cc.) were introduced into the reaction mixture, and on further heating for about one-half hour the allyl starch was in solution. It was then steam distilled and purified as described above. An average yield of five preparations was 861 g., or 90 percent of theoretical, and the substitution of the product was 1.6 allyl groups per glucose unit. An attempt was made to reduce further the amount of water in the reaction mixture by adding half the amount of alkali required as 50 percent solution and the other half as solid flakes. The average result of three experiments was: Yield, 813 g., or 84 percent, substitution, 1.65 groups. The decrease in yield and only slight increase in substitution were due to the difficulty of stirring a mixture containing little liquid. The method was therefore further modified by adding part of the acetone (500 cc.) to the reaction mixture, which was then as follows: Starch, 800 g., allyl chloride, 985 g.; 50 percent sodium hydroxide, 490 g.; solid sodium hydroxide, 245 g.; sodium iodide, 8 g.; acetone, 500 cc. The rest of the acetone was added with the acid after the etherification reaction was complete. The average for three preparations was: Yield, 927 g., or 92 percent; substitution, 1.8 allyl groups per glucose unit.

Preparation of methallyl starch is described by Nichols, Wrigley, and Yanovsky (42).

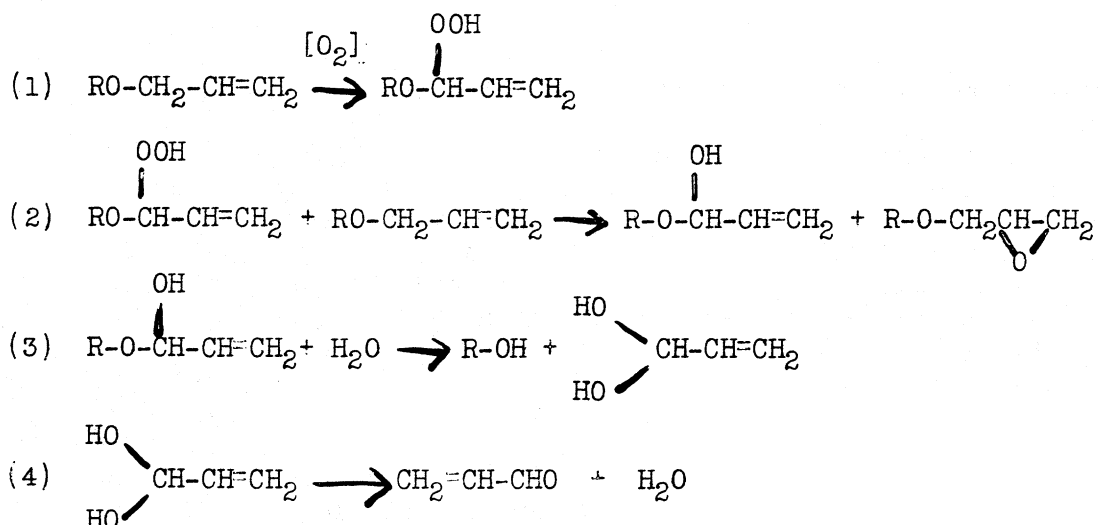
## Physical and Chemical Properties of Allyl Starch

The gummy allyl starch prepared by any of the above methods is soluble in alcohols, ketones, aromatic hydrocarbons, and a number of other organic solvents. It is insoluble in aliphatic hydrocarbons. In some solvents or mixtures of solvents concentrated solutions allyl starch can be prepared (40-60%). Allyl starch solutions are quite stable. On the other hand, if the gummy allyl starch is left in the air it soon becomes coated with a hard insoluble material. This can be avoided by keeping allyl starch under water at a comparatively low temperature. The formation of insoluble coating is due to oxidation by the oxygen of the air and the subsequent cross-linkage polymerization of the partly oxidized compounds. This reaction is catalyzed by heat, ultraviolet radiation and paint driers. Quantitative results on insolubilization of thin films of allyl starch under different conditions are given in Tables III and IV (38, 48).

The results clearly show the influence of temperature on the rate of insolubilization (curing). The effect of cobalt drier was more striking at room temperature than at elevated temperatures. When ultraviolet radiation was used as a source of heat addition of cobalt drier produced no further improvement.

The study of the mechanism of the oxidation and polymerization of such a complex material as allyl starch presents many difficulties. Fortunately a number of allyl ethers of comparatively simple polyhydroxy compounds can be readily prepared and purified. They seem to polymerize in the same manner as allyl starch. Absorption of oxygen during polymerization was studied quantitatively for allyl ether of methyl glucoside, mannitol, sorbitol, and other polyhydroxy compounds (10, 42). The course of polymerization was studied by heating the ethers in a modified Ostwald pipette through which oxygen was passed at a uniform rate until the liquid gelled to a colorless transparent resin (36, 37).

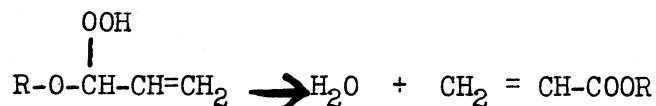
During this polymerization process a number of physical and chemical changes take place. Among the physical changes observed are an increase in density, refractive index and viscosity. As mentioned previously, cobalt driers (also 47) and ultraviolet radiation catalyze the polymerization of allyl ethers. On the other hand, alkalis and organic bases inhibit such polymerization. Chemical changes include the formation of peroxide, epoxide, and acrolein. The latter can be distilled off and identified by means of its 2,4-dinitrophenylhydrazine. If one accepts the theory of Criegee, Pilz and Flygare (13) and of Farmer and Sundralingam (18) on the autoxidation of olefinic compounds, there is a rather simple explanation for the positive peroxide and epoxide test and the formation of acrolein. The following equations would represent the course of the reaction (37):



The first step shows formation of the hydroperoxide at the  $\alpha$ -methylenic carbon which in this case should be especially reactive, since it is both adjacent to an ether oxygen and in  $\alpha$ -position to a double bond. The second step shows decomposition of the peroxide according to the scheme suggested by Farmer and Sundralingam, in which the hydroperoxide oxidizes a double bond with the formation of an epoxy group. These two equations represent the application of Farmer's ideas to allyl ethers. The hydroxy compound formed as a result of step two is a hemiacetal, which would be readily hydrolyzed if a trace of water were present. It is evident from equations 3 and 4 that a trace of water is all that is necessary for complete hydrolysis of any amount of hemiacetal formed, and according to Farmer's findings and the authors' observations, water is formed during oxidations of this type. The formation of epoxy groups in the above-suggested scheme of oxidation and the well-known ease with which epoxy compounds polymerize add to the plausibility of this mechanism.

There is some evidence, however, that more than one reaction takes place during the polymerization of allyl ethers. Besides, the above suggested scheme does not explain all the phenomena observed during polymerization. Thus, for instance, formation of water is not explained, although the experimental evidence indicates that more than a trace of water is formed during the oxidative polymerization. By actual analysis in one case over 0.5 percent of the original ether was identified as water. Another plausible mechanism for polymerization of allyl ethers was therefore suggested (68).

Clover (12) found that hydroperoxides of ethers can break down, with the formation of an ester and water. In the case of ethyl benzyl ether hydroperoxide the principal decomposition product was ethyl benzoate. It is evident that if a similar reaction takes place in allyl ethers, it will proceed according to equation



In other words, formation of acrylic ester might be expected.

This hypothesis was put to a test. Allylmannitol (113 g.) was heated at 80° while oxygen was passed through the liquid. The process was stopped at about three-quarters of the way to gelation. Determination of ester equivalent gave the figure 764, corresponding to 9.3 percent acrylate, or about 0.5 acrylate group per mole of the original allylmannitol. An attempt to identify the

TABLE III

INSOLUBILIZATION OF ALLYL STARCH FILMS WITH  
AND WITHOUT COBALT NAPHTHENATE

Sample No.	Drier % Co	Temp. °C.	Type of Heating	% Insoluble material after:						
				1 hr.	2 hr.	3 hr.	4 hr.	5 hr.	6 hr.	24 hr.
1	...	120	Oven	...	100	...	...	...	...	...
2	...	120	Oven	...	100	...	...	...	...	...
3	...	100	Oven	...	86	94	99	100	...	...
	0.4		Oven	...	93	93	95	96	97	97
	0.2		Oven	...	87	93	...	100	...	...
	...		Infrared	78	97	99	100	...	...	...
	0.4		Infrared	...	91	95	100	...	...	...
	0.2		Infrared	...	91	93	97	100	...	...
	...		...	...	...	...	...	...	...	...
4	...	100	Oven	80	89	96	98	100	...	...
	0.4		Oven	95	96	99	100	...	...	...
	0.2		Oven	95	95	100	...	...	...	...
	...		Infrared	91	96	100	...	...	...	...
	0.4		Infrared	93	96	100	...	...	...	...
	0.2		Infrared	89	97	100	...	...	...	...
	...		...	...	...	...	...	...	...	...
5	...	100	Oven	86	95	97	98	100	...	...
	0.4		Oven	88	92	92	97	...	100	...
	0.2		Oven	91	92	94	97	99	100	...
	...		Infrared	88	95	100	...	...	...	...
	0.4		Infrared	89	92	94	97	100	...	...
	0.2		Infrared	91	...	100	...	...	...	...
	...		...	...	...	...	...	...	...	...
6	...	100	Oven	83	95	99	99	100	...	...
	0.4		Oven	93	93	95	100	...	...	...
	0.2		Oven	91	92	92	100	...	...	...
	...		Infrared	89	97	100	...	...	...	...
	0.4		Infrared	92	96	100	...	...	...	...
	0.2		Infrared	89	93	99	100	...	...	...
	...		...	...	...	...	...	...	...	...
7	...	80	Oven	...	...	79	81	83	88	100
	0.4		Oven	...	...	92	95	95	99	100
	0.2		Oven	...	...	94	95	96	99	100
	...		Infrared	...	...	87	94	97	98	100
	0.4		Infrared	...	...	92	97	98	99	100
	0.2		Infrared	...	...	94	94	97	99	100
	...		Ultraviolet	...	...	96	100	...	...	...
	0.4		Ultraviolet	...	...	91	99	100	...	...
	0.2		Ultraviolet	...	...	92	95	96	96	...
	8		...	80	Oven	...	79	87	88	94
0.4		Oven	89		90	93	...	94	97	100
0.2		Oven	91		94	94	95	95	95	100
...		Infrared	77		91	96	99	99	100	...
0.4		Infrared	88		93	96	99	99	100	...
0.2		Infrared	90		...	96	...	97	98	100
...		Ultraviolet	88		92	98	98	99	...	...
0.4		Ultraviolet	88		89	96	99	100	...	...
0.2		Ultraviolet	89		93	94	100	...	...	...

TABLE IV

INSOLUBILIZATION OF ALLYL STARCH FILMS AT  
ROOM TEMPERATURE

Sample No.	Drier, % Co	% Insoluble Material after:			
		1 week	2 weeks	3 weeks	4 weeks
9	...	55	73	73	77
	0.4	91	99	99	100
	0.2	94	96	99	99
10	...	16	...	70	73
	0.4	99	100	...	...
	0.2	99	100	...	...
11	...	...	...	80	82
	0.4	98	100	...	...
	0.2	98	100	...	...
12	...	13	54	72	76
	0.4	98	100	...	...
	0.2	97	100	...	...
13	...	73	77	80	81
	0.4	88	100	...	...
	0.2	91	99	99	100

acrylic acid as its p-bromophenacyl ester was unsuccessful, perhaps because most or all of the acrylate was in a polymerized state. Acrylic ester, if present, probably takes part in the polymerization of allyl ethers. It is believed in the absence of further work that perhaps both of the above suggested mechanisms take part in the polymerization.

The possibility of using organic peroxides, such as benzoyl peroxide or t-butyl hydroperoxide as catalysts in the polymerization of allyl ethers has been investigated. Early experiments (36) showed, however, that such peroxides (in quantities of 1 to 5%) on heating with allyl ethers at 80-100° produced only a slight increase in the viscosity of the ethers. Only in a few experiments when an enormous excess (over 15%) of benzoyl peroxide was gradually added (at 97°) gelation of allyl ethers was achieved. It is possible, therefore, that carbon to carbon polymerization of allyl ethers might be catalyzed by the continually generated hydroperoxides. This and the other two mechanisms described might proceed simultaneously.

The question of the function of organic peroxides has been recently reinvestigated by Zief (79), who was primarily interested in polymerization of allylsucrose. Besides the two peroxides mentioned, Zief used also di-t-butyl peroxide, 2,2-bis(t-butylperoxy) butane, and cumene hydroperoxide. When allylsucrose was heated for 2 hours with 2 percent of these peroxides at 100° there was in all five cases only a slight increase of viscosity. Much larger increase in viscosity was observed when the mixtures were heated at 135°, and under these conditions allylsucrose with 2 percent cumene hydroperoxide gelled in 65 minutes. But when allyl ethers of mannitol and pentaerythritol were heated for two hours at the same temperature and with the same amount of cumene hydroperoxide only a slight increase in viscosity of these ethers was noted. Further work with allylsucrose showed that different samples of allylsucrose behaved differently with cumene hydroperoxide. Thus a sample prepared in a stainless steel container gelled more rapidly than one prepared in a monel metal container, and the latter gelled more rapidly than the product made in glass. Also, one sample which gelled with cumene hydroperoxide in 65 minutes showed after distillation only a slight increase in viscosity after two hours. It appears as if some impurity in the allylsucrose preparations might act as a cocatalyst with cumene hydroperoxide. But other factors might be responsible for the odd behavior of allylsucrose with cumene hydroperoxide. Obviously this subject requires further study.

Besides its ability to polymerize in the presence of oxygen allyl starch can be polymerized or "vulcanized" with sulfur. The usual procedure is to compound the gummy allyl starch on an ordinary rubber mill with sulfur, accelerators and other compounding ingredients and cure it at an elevated temperature (38, 45). A typical example of such a compound is given in Table V.

TABLE V. FORMULATION FOR CURING ALLYL STARCH WITH SULFUR

	Parts
Allyl starch	10
Sulfur	0.5
Zinc oxide	0.5
Titanium dioxide	0.3
Stearic acid	0.2
Mercaptobenzothiazole	0.05
Tetramethylthiuram disulphide	0.1
Organic dye (Heliogen Green, Sudan Red, or any suitable dye)	0.014

The compounded mixture was cured for 5 minutes in a mold at 125° C. to form a slab 0.040 inch in thickness. The plastic material thus obtained is, like the polymerized allyl starch films, insoluble in organic solvents. While oxidation polymerization of allyl starch is applicable to surface or thin films of allyl starch, sulfur polymerization acts throughout the bulk of allyl starch.

Another method of polymerizing allyl starch applicable to both surface and bulk polymerization is available. This method consists in treating allyl ethers with sulfur chloride or sulfur dichloride (72). The reaction is violent but can be moderated by proper regulation of the temperature or the concentration of the reacting substances. Thus a dilute solution of sulfur chloride in benzene can be added to a dilute solution of allyl starch in benzene. Wooden panels coated with mixed solution were dried at room temperature. After about 3.5 hours the coat was insoluble in acetone. A better way of curing allyl starch films is to expose them to vapors of sulfur chloride or sulfur dichloride. After a few hours of exposure the films are insoluble in organic solvents. The following is an example of bulk polymerization: 2.3 g. of sulfur monochloride dissolved in 5 cc. of toluene were gradually added, at room temperature, to 20 grams of 25 percent solution of allyl starch in toluene with swirling to prevent local precipitation. The flask containing the mixture was then stoppered and placed in an ice water bath. The mixture solidified after 15 minutes. The flask was allowed to stand overnight in a cold room. The stopper was then removed and the toluene evaporated. The solid residue was insoluble in organic solvents.

#### Potential Uses of Allyl Starch

The ability of allyl starch to polymerize to a thermosetting plastic, the resistance of the polymerized material to solvents, oils and heat up to 200° C., its compatibility with a number of resins and plasticizers, and its ability to copolymerize with simpler allyl ethers and other monomers (46, 59) suggest a

number of practical applications (2, 24, 38, 39, 40, 49, 51, 52). The most obvious application is the use of allyl starch as lacquer or varnish for furniture and other wood products. To dissolve allyl starch (the gummy material contains 25-30% water) in organic solvent the water must be removed by some drying procedure or by azeotropic distillation with water immiscible solvent. Dry allyl starch can also be obtained from a solution of allyl starch by precipitating it with a miscible nonsolvent or by spray drying (16). A film of allyl starch deposited on a suitable surface will dry to touch in a very short time (10-30 mins.). Such a film, however, possesses a low distensibility and gradually develops a fine pattern of cracks. Addition of a suitable plasticizer eliminates this defect.

A typical brushing lacquer formulation is given in table VI (15).

TABLE VI. ALLYL STARCH COATING COMPOSITION

	Parts
Allyl starch	100
Paraplex RG-7 <sup>1</sup>	50
Ethanol	10
Butanol	10
Butyl cellosolve	20
Xylene	130
Cobalt drier <sup>2</sup>	0.1

1/ Made by Rohm and Haas Co., Philadelphia, Pa. The mention of commercial products in this paper does not imply that they are endorsed or recommended by the Department of Agriculture over others of a similar nature not mentioned.

2/ Cobalt naphthenate or octoate; 0.1% cobalt metal on dry allyl starch.

Another formulation consists of the following ingredients (49).

TABLE VII. ALLYL STARCH COATING COMPOSITION

	Parts
Allyl starch	85
P-10 (Baker Castor Oil Co.) or ) Glyceryl monoricinoleate )	15
Cobalt drier	0.1

Dissolved in alcohol to desired concentration.



Various other formulations for wood and metal coating and for other uses are suggested in references 3, 15, 24, and 52. Data on the compatibility of various resins and plasticizers with allyl starch are given in references 3 and 24.

Among other suggested or actual uses of allyl starch are: As a vehicle for printing inks, particularly for printing on cellophane and glassine paper (3); for coating or impregnating paper and textiles; as shellac replacement; as a modifier for other lacquers and varnishes; for metal finishes; as a thermosetting adhesive; as an ingredient of bronzing liquids; as a wood sealer, and for miscellaneous other purposes (24).

### Derivatives of Allyl Starch

While allyl starch exhibits some properties desirable for coating compositions and other uses, it has some drawbacks limiting its uses. Because of its insolubility in aliphatic hydrocarbons, allyl starch--like many other resins--requires the use of more expensive solvents. More important is the sensitivity of allyl starch coatings to water and other aqueous liquids, barring their use for outside coatings. It is believed that these drawbacks are due partly to the ether linkage of allyl starch, and more so to the residual unsubstituted hydroxyl groups left in allyl starch. To test the validity of these assumptions for allyl starch a number of mixed saturated alkyl-allyl mixed ethers were prepared (29). The alkyl groups varied from ethyl to heptyl and also included lauryl. The results showed that as the length of the chain and the degree of substitution with the alkyl groups increased the solubility of mixed ethers in alcohol decreased and they became soluble in Skellysolve B and n-heptane. Thus mixed ethers of substitution 1.4 allyl and 1.5 butyl groups, or 1.6 allyl and 1.3 amyl, or 2.0 allyl and 0.9 lauryl were soluble in Skellysolve B and n-heptane but insoluble in alcohol. In another study of mixed ethers (62) ethyl, butyl, amyl, benzyl, o-chlorobenzyl, and p-chlorobenzyl allyl ethers of starch were prepared. Films of these ethers were cured at 100° and 150° C. and actually tested for their resistance to various test solutions such as water, soap solutions, dilute solutions of sodium and ammonium hydroxide, 50 percent alcohol and others. The tests showed that mixed allyl ethers containing benzyl, o-chlorobenzyl, and p-chlorobenzyl groups had somewhat better resistance to the test solutions than the control and other mixed ethers.

With the same object in view a number of mixed ether esters were prepared. French investigators (11) prepared allyl starch acetate and allyl starch laurate primarily with the view of obtaining films with better plasticizing properties. In this Laboratory allyl starch acetate, propionate, laurate, stearate, oleate, linoleate, allyl carbonate, benzoate, and phenyl carbamate were prepared (56, 57). Cured films were tested for resistance to various aqueous liquids in the same manner as those of mixed ethers. Most improvement was shown by mixed ether-esters with a long chain ester groups, such as allyl starch laurate and allyl starch stearate. But these allyl starch esters require a long curing time even at elevated temperature.

Another attempt to improve water resistance of allyl starch films was made by preparing a copolymer of allyl starch and styrene. The copolymer was made by heating toluene-butanol solution of allyl starch with dipentene solution of styrene in the presence of cumene hydroperoxide (69). Films of styrenated allyl starch cured at elevated temperatures showed somewhat better resistance to various

test solutions than the untreated allyl starch. Films cured at room temperature were, however, not better than those of control allyl starch.

### Allyl Starch Emulsions

For certain uses of allyl starch, such as coating of paper or textiles, properly compounded solutions of allyl starch can be used. In order to operate such a process economically, solvent recovery equipment must be installed. To save on this extra equipment and to avoid the fire hazard connected with the use of volatile solvents the paper and textile processors use as much as possible aqueous solutions or dispersions. To meet this demand allyl starch emulsions were prepared (58, 71, 73). One series of emulsions contained allyl starch, plasticizer, emulsifier, water and some solvent. In another series of emulsions the solvent was eliminated entirely. Samples of such formulations are given in Table VIII.

TABLE VIII. SOLVENT-FREE EMULSIONS OF ALLYL STARCH

Formulation No.	1	2
Allyl Starch, g.	80	85
Flexol TWS, g.	20	15
Triton X-100, g.	5	5
NH <sub>4</sub> OH, conc., ml.	1-3	2
Water, total, g.	100-170	100-170

The laboratory-scale preparation of these emulsions is conveniently carried out in a 500-ml. three-necked flask equipped with wire stirrer, reflux condenser, and a system for maintaining a nitrogen atmosphere. A stirring motor having two or three gear ratios is useful for this work. Enough allyl starch solids of 30 percent water content to afford the indicated quantities of dry-basis resin is ground with a mortar and pestle and charged to the flask. After the plasticizer has been stirred in and a nitrogen atmosphere established, the flask is set in a 90° C. bath, where blending of the allyl starch and plasticizer is continued for one hour. The emulsifier and ammonia are then added, and the mixture is stirred for 15 minutes. Finally the flask is transferred to a cooler bath--25, 40, or 60° C.--and water is slowly added from a dropping funnel in accordance with the inversion technique, finishing as an oil-in-water emulsion. Allowance is made for the water content of the allyl starch solids used. The viscosity of the blend of allyl starch, plasticizer, and emulsifiers governs the temperature of the bath during the addition of water. Forty degrees centigrade is most generally satisfactory.

Since different batches of the allyl starch may vary slightly in substitution, molecular weight, and acidity, small variations in formulation or technique are sometimes necessary. Since a final pH of 8 to 10 is most satisfactory, some batches require the use of 2 or 3 ml. of concentrated ammonia instead of one. With some batches, the minimum water content of the finished emulsion must be 130, 150, or 170 grams instead of 100. With the higher contents of water, addition of a dispersing agent--Alkanol S, for example--gives smoother films.

Emulsions of this type are generally stable for 6 months or more. They yield clear, glossy films by either air-drying or baking.

In shipping emulsions a considerable portion of freight charge is due to water. To reduce this expense an emulsifiable paste has been prepared. This paste can be converted into emulsion by incorporating the proper amount of water.

### Improving Curing Time of Allyl Starch

When deposited on wood films of allyl starch (containing cobalt drier) become dry to the touch in a very short time, depending upon the solvent used. Then they gradually cure and harden. After about 24 hours at room temperature the films are ready for rubbing and application of the second coat. This procedure is not quite satisfactory to furniture manufacturers who prefer to put on two or three coats in one day. Attempts were made, therefore, to accelerate the cure of allyl starch. A number of potential catalysts were tested for this purpose. The only chemical catalysts, outside of metallic paint driers, that showed some improvement in the rate of cure were esters of itaconic acid (dimethyl, diethyl, and dibutyl esters) (7).

The best results thus far were obtained on irradiation (without heat) of allyl starch films with ultraviolet rays. Under these conditions the degree of hardness, measured with Sward Rocker, obtained in 4 to 6 hours was equal to that reached by the control in 24 hours. Moreover, when using ultraviolet radiation, addition of cobalt drier was unnecessary (64).

### Storage of Allyl Starch

As stated previously, solid gummy allyl starch is gradually oxidized in the air with the formation of insoluble material. It is therefore kept under water to protect it from the oxygen of the air. But even with this precaution the amount of insoluble material increases considerably on long storage. Thus in case of one batch 20 percent of the material was insoluble after seven months' storage. Addition of certain chemicals to the water delayed considerably the changes taking place during the storage (64). After storing allyl starch at room temperature under water containing glucose, or ammonia, or diethylamine (about 2% on allyl starch solids) for seven months the product remained completely soluble in organic solvents and cured as well as the original allyl starch. After 13 months' storage allyl starch under glucose solution still behaved like the original product, samples under solutions of ammonia and diethylamine contained only a small amount of insoluble material.

### Toxicity of Allyl Starch

Cellophane or glassine paper with legends printed with ink containing allyl starch are used for wrapping some food products (candies, e.g.). Sometimes the paper itself is coated with allyl starch. The knowledge of pharmacological properties of allyl starch is obviously important. A summary of the results by the authors of the forthcoming article on the subject (1) is as follows:

"Albino rats were fed diets containing 0.5, 1.0, 2.0, and 4.0 percent polymerized allyl starch for 400 days. A slight inhibition in growth was found on the three highest dosage levels, but the significance of the difference from controls was doubtful. At time of autopsy all tissues appeared normal, but upon histopathological examination two changes were found in the animals on diets containing 4 percent allyl starch. There was evidence of a mild inflammatory reaction in the pyloric zone of the stomach, and in the females an absence of corpus luteum formation in the ovaries. Thus the tests indicate that while allyl starch should not be incorporated in food products in appreciable amounts, such traces as might be transferred to a product packaged in coated paper would not constitute a health hazard."

### Allyl and Methallyl Derivatives of Other Polyhydroxy Compounds

As mentioned earlier in this paper simpler allyl derivatives of polyhydroxy compounds were used to study the mechanism of polymerization of allyl ethers. It is outside of the scope of this review to describe the preparation and properties of such compounds. But it seemed advisable to give a list of polyalcohols with known allyl derivatives of various degree of substitution and of references pertaining to these compounds. It is believed that the list is complete, but in a work of this type omissions are quite often inevitable.

#### Carbohydrate Polymers:

Cellulose 8<sup>1/</sup>, 14, 28, 30, 54, 65, 66.  
Inulin 66  
Pectin 17

#### Sugar Alcohols:

Glycerol 4, 23, 37, 42<sup>1/</sup>, 67, 68  
Erythritol 68  
Arabitol 68  
Xylitol 68  
Dulcitol 68  
Iditol 68  
Mannitol 23, 37, 42<sup>1/</sup>, 68<sup>2/</sup>  
Sorbitol 37, 42<sup>1/</sup>  
Talitol 68

#### Sugars:

Galactose 5<sup>3/</sup>, 50<sup>3/</sup>, 60<sup>4/</sup>  
Glucose 6<sup>3/</sup>, 19<sup>3/</sup>, 20<sup>3/</sup>, 22<sup>5/</sup>, 23, 60<sup>4/</sup>  
Fructose 23  
Maltose 23  
Sucrose 21, 23, 26, 27, 37, 39, 40, 42<sup>1/</sup>, 44, 47, 53, 55, 57, 66, 70, 74, 75, 76, 77, 78, 79

#### Various Polyalcohols:

Butylene Glycol 37  
Ethylene Glycol 37, 42<sup>1/</sup>  
Di- and triglycerol 67  
Pentaerythritol 37, 42<sup>1/</sup>  
Dipentaerythritol 42<sup>6/</sup>  
 $\alpha$ -methyl glucoside 36, 66  
Inositol 37  
Dianhydromannitol 25  
Dianhydrosorbitol 25

1/ METHALLYL DERIVATIVE; 2/ MON-, DI-, AND TETRAALLYL DERIVATIVES; 3/ ALLYLGLYCOSIDES;  
4/ ALSO GLYCOSIDES; 5/ 3-ALLYLGLUCOSE; 6/ ALSO METHALLYL DERIVATIVE.

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